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14. ABSTRACT

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15. SUBJECT TERMS

Boron Nitride Nanotubes, composite materials, Aluminum Alloys , Titanium Alloy, Theoretical Chemistry

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Final Report for AOARD Grant 134071 "Composite reinforcement using boron nitride nanotubes"

9 May, 2014

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Abstract: Boron nitride nanotubes have been proposed as a suitable reinforcement for metal matrix composites. In order to be effective, the interaction between the metal and the nanotube needs to be strong while retaining the nanotube structure. Computational quantum chemistry was used to study interactions of aluminium and titanium metal clusters with boron nitride nanotubes. The effect of varying the radius of the nanotubes and the size of the aluminium and titanium clusters was considered. In addition, the strength and nature of the binding to both pristine and defective boron nitride nanotubes was compared. It was found that even though strong binding occurred, particularly with titanium, the structure of the nanotubes was not greatly disrupted. This behaviour is advantageous for their use as reinforcement materials. Defects created by removing a boron or nitrogen atom from the nanotube enhance binding had different qualitatively effects on the change in bond strength with nanotube radius.

Introduction:

Nanotubes have been proposed for use as a reinforcing material in metal matrix composites due to their potential to produce light-weight, high-mechanical-strength materials. Although substantial work has been carried out using carbon nanotubes (CNTs),[1] it has been proposed that boron nitride nanotubes (BNNTs) might be preferable due to their higher chemical stability and reduced tendency to cluster.[2] This proposal has been supported by results that were obtained with BNNTs and aluminium (Al).[3] Based on consideration of experimental results and thermodynamic modelling, it was concluded that formation of a strong bond between the matrix and the boron nitride reinforcement was possible, without disrupting the structure of the nanotube significantly. If nanotubes are to improve the tensile strength of a metal matrix composite, the bonding between metal matrix and the nanotube must occur.

Therefore one of the key factors in determining whether or not boron nitride will be a useful reinforcement material is the strength of binding between the nanotube and the metal. The binding has to be sufficiently strong to provide good reinforcement, without disrupting the structure of the nanotube. The strength of bonding between the metal matrix and nanotube was one of the issues investigated in this project.

It has also been found that modified or defective carbon nanotubes behave differently as a reinforcing materials.[4] Carbon nanotubes and metals generally interact quite weakly, and for a (8,0) single walled nanotube Durgun *et al*. obtained the following results using quantum chemical calculations: Cu 0.7 eV; Fe 0.8 eV; and Ti 2.2 eV.[5] Similar figures have been obtained for (5,5) and (6,6) nanotubes. However, the binding energy can be considerably increased by

introducing defects into the carbon nanotubes. Zhuang *et al*. showed that by removing an atom from a carbon nanotube, a metal ion will generally strongly bind near the defect – with chemical bonding occurring in some cases: Cu 3.27 eV; Fe 6.31 eV; and Ti 7.57 eV.[4] In order to ensure that the strength of the metal matrix composite is maintained under extreme mechanical conditions, this interaction must be strong and should not fail, so consideration of defective nanotubes in selection of a reinforcing material should be considered. This project therefore considered if a similar scenario occurs for the BN nanotubes.

The strength of the interaction between a nanotube and a single atom can differ quite significantly from the interaction strength of the a nanotube and layers of metal atoms.[9] This can even result in different trends in the relative strengths of bonding to different metals. Therefore in order to determine the most appropriate composition of a metal matrix composite, structures of different sizes must be considered. In this study, preliminary results in this direction were obtained by considering the interactions of the nanotubes with small clusters of 1 – 4 metal atoms

Experiment:

Quantum chemical density functional theory calculations were used to investigate the utility of BNNTs as a reinforcement material in metal matrix composites. Pristine and defective nanotubes of various radius, and clusters of 1-4 atoms of Al or titanium (Ti) atoms were considered. Nanotubes with indices from (5,5) to (10,10) were considered, and were periodic in the direction of their axis. First-principles density-functional theory plus dispersion (DFT-D) calculations were carried out using the DMol3 module in Materials Studio.[7] The BNNTs and metal clusters were fully optimized in the given symmetry using the generalized gradient approximation[8] treated by the Perdew-Burke-Ernzerhof exchange-correlation potential with long rang dispersion correction via Grimme's scheme.[9] An all electron double numerical atomic orbital augmented by *d*-polarization functions (DNP) was used as the basis set. These approaches have been demonstrated to provide accurate predictions of binding energies and configurations of these types of system.
The lengths of the optimized BNNTs with indices from (5,5) to (10,10) were between 12.585 ~ 12.590 Å, which is long enough to avoid interactions between periodic images. Clusters of 1 to 4 aluminium or titanium atoms were optimized and placed a various positions close to the optimised BNNT strucutre. Further optimisations were then carried out starting from 5 different initial positions of the clusters, and the minimum energy structure selected. The binding energy, E_b, was determined from the difference in the energy of the metal cluster bound to the nanotube, E_{M_n-BNNT}, and the nanotube, E_{BNNT}, and cluster energy, E_{M_n}:

$$E_b = E_{M_n-BNNT} - (E_{BNNT} + E_{M_n}) \quad (1)$$

where M is either Al or Ti and n is the number of atoms in the cluster.
This process was then repeated with one B or one N atom removed from the BNNT unit to give a defective nanotube.

Results and Discussion:

Table 1 gives the binding energies between the pristine nanotubes and a single metal atom for BNNTs of various radii. Ti is found to bond more strongly to the BNNT, resulting in shorter bond distances and greater charge transfer. Note that in the tables, a positive value of the charge transfer indicates that electrons are transferred from the metal to the BNNT. The Al atom binds to both the N and B atoms with the Al-B and Al-N distances being similar. The Ti atom interacts more strongly with the N atom. Figure 1 shows the configuration of the Al and Ti atoms on the (5,5) BNNT. In both cases the charge transfer, binding energies and bond distances decrease as the radius of the BBNT increases, indicating that higher curvature of the nanotube promotes bonding with the metal atoms.

The binding of clusters of up to 4 atoms to the (5,5) BNNT was also considered. For Al, the binding energy increased from 0.67 eV with a single Al atom to 1.22 eV with 4 atoms. The structure of the Al tetramer was optimized before it was allowed to interact with the BNNT and formed a planar structure. The structure was slightly distorted on bonding, and some of the Al atoms interacted with the B atoms while others interacted with the N atoms. The configuration of the tetramer interacting with the BNNT is shown in Figure 1c). For Ti, the tetramer forms a tetrahedral structure which is maintained on bonding with the BNNT. In this case there is an increased strengthening of the interaction with an increase in Ti atoms, increasing from 1.71 eV with one Ti atom to 4.23 eV with the tetramer. The base of the tetrahedral cluster binds with the BNNT with the three Ti atoms interacting strongly with the N atom of the nanotube.

Table 1. Binding energies (eV), bond distances (Å) between the Al or Ti and the N or B atoms of the BNNT, and charge transfer from the metal to the BNNTs. Note that positive CT (e) indicates electron transfer from the metal to the BNNT.

BNNT index	Al			
	Bond energies (eV)	Al-B(Å)	Al-N(Å)	CT(e)
(5, 5)	0.67	2.339	2.388	0.127
(6, 6)	0.61	2.346	2.408	0.121
(7, 7)	0.57	2.351	2.426	0.117
(8, 8)	0.56	2.370	2.457	0.115
(9, 9)	0.54	2.370	2.460	0.112
(10, 10)	0.52	2.370	2.467	0.108
	Ti			
	Bond energies (eV)	Ti-B(Å)	Ti-N(Å)	CT(e)
(5, 5)	1.71	2.281	1.996	0.338
(6, 6)	1.62	2.286	1.981	0.328
(7, 7)	1.54	2.299	1.980	0.313
(8, 8)	1.51	2.304	1.992	0.309
(9, 9)	1.40	2.305	2.011	0.304
(10, 10)	1.35	2.322	2.000	0.284

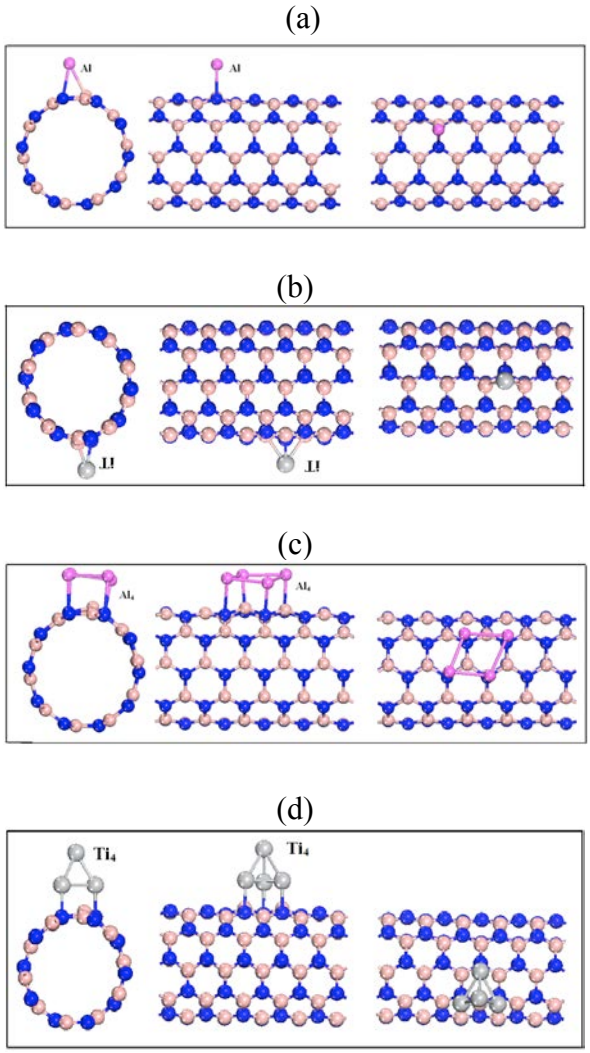

Figure 1. Configurations for binding of Ti and Al atoms and tetramers to a (5,5) BNNT: a) a single Al atom; b) a single Ti atom; c) an Al tetramer; d) a Ti tetramer.

The binding energies, bond distances and charge transfer for Al interacting with defective nanotubes is shown in Table 2. It is interesting to note that some trends differ when the N atom is removed instead of the less electronegative B. When there is a N defect, the Al binds to the three B atoms near that defect, and when there is a B defect, the Al binds to the three N atoms near that defect. The binding between the Al and the defective BNNT is greatly enhanced compared to the pristine BNNT in all cases, with electron transfer to the Al from the BNNT when a N is removed, but from the Al when B is removed. Binding is particular strong in case of a B defect. In addition, the binding increases with the radius of the nanotube when there is a B defect, unlike the case with a N defect or for the pristine nanotubes. Figure 2 shows the optimized configurations, and we note that the Al is essentially incorporated into the BNNT when there is a B defect. We also note that the structure of the BNNT is not disrupted.

Table 2. Binding energies (eV), bond distances (Å) between the Al and the B or N atoms of defective BNNTs, and charge transfer (e) from the metal to the BNNTs. The BNNT either have a missing N or B atom.

BNNT index	With N defect				
	Binding energies (eV)	Al-B1(Å)	Al -B2(Å)	Al -B3(Å)	CT(e)
(5, 5)	2.66	2.302	2.286	2.178	-0.112
(6, 6)	2.59	2.292	2.293	2.170	-0.114
(7, 7)	2.55	2.298	2.291	2.167	-0.112
(8, 8)	2.51	2.295	2.291	2.161	-0.114
(9, 9)	2.49	2.303	2.279	2.158	-0.110
(10, 10)	2.48	2.291	2.297	2.158	-0.111
	With B defect				
	Binding energies (eV)	Al-N1(Å)	Al-N2(Å)	Al -N3(Å)	CT(e)
(5, 5)	8.47	1.758	1.758	1.787	0.814
(6, 6)	8.56	1.754	1.754	1.782	0.806
(7, 7)	8.62	1.752	1.752	1.777	0.795
(8, 8)	8.68	1.751	1.751	1.775	0.790
(9, 9)	8.72	1.750	1.750	1.771	0.777
(10, 10)	9.70	1.749	1.749	1.770	0.777

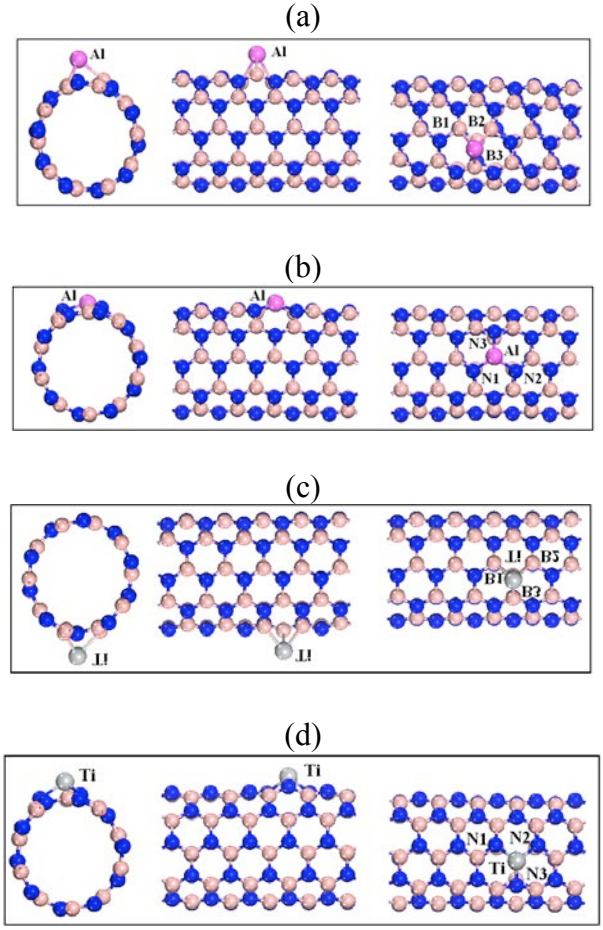

Figure 2. Configurations for binding of an Al atom to defective BNNTs: a) defective BNNT has a missing N atom; b) defective BNNT has a missing B atom.

Results were also obtained for the interaction between a Ti atom and defective BNNT's. Again, the binding is considerably enhanced, and stronger binding occurs with an increase in radius of the BNNT for the case where there is a B defect. The electron density is always lower on the Ti due to the greater electronegativity of both the B and N compared to Ti. Figure 2 c) and d) show the configurations obtained. The Ti is not as well integrated into the B defective BNNT structure as in the case of the Al, and the BNNT structure is slightly disrupted. This reflects the smaller atomic radius of Al compared to Ti.

Table 3. Binding energies (eV), bond distances (Å) between the Ti and the B or N atoms of defective BNNTs, and charge transfer (e) from the metal to the BNNTs. The BNNT either have a missing N or B atom.

BNNT index	With N defect				
	Binding energies (eV)	Ti-B1(Å)	Ti-B2(Å)	Ti-B3(Å)	CT(e)
(5, 5)	4.56	2.130	2.130	2.206	0.198
(6, 6)	4.51	2.134	2.134	2.198	0.187
(7, 7)	4.46	2.135	2.135	2.198	0.183
(8, 8)	4.44	2.136	2.136	2.193	0.182
(9, 9)	4.43	2.137	2.137	2.186	0.184
(10, 10)	4.40	2.139	2.139	2.182	0.179
	With B defect				
	Binding energies (eV)	Ti-N1(Å)	Ti-N2(Å)	Ti-N3(Å)	CT(e)
(5, 5)	10.03	1.896	1.896	1.951	0.892
(6, 6)	10.07	1.895	1.895	1.944	0.890
(7, 7)	10.11	1.894	1.894	1.940	0.886
(8, 8)	10.15	1.893	1.893	1.937	0.883
(9, 9)	10.19	1.893	1.893	1.933	0.882
(10, 10)	11.14	1.893	1.893	1.930	0.878

The results demonstrate that strong binding of Al and Ti with BNNTs can be obtained, and that this is obtained with little disruption to the BNNT structure. When defects are present in the tubes, the binding becomes stronger, and Al or Ti atoms are incorporated into the structure of the BNNT to repair the defect.

These results are consistent with the proposal that BNNTs will perform well as reinforcement in metal matrix composites, however further work is required. Extension of these fundamental studies are required to examine the effects of using nanotubes of different chiralities, interaction with larger Al and Ti clusters and lattices and use of double-wall nanotubes. In addition, consideration of issues that become important in the fabrication process, such as effects of oxygen and tensile strength will be important.

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List of Publications and Significant Collaborations that resulted from your AOARD supported project: In standard format showing authors, title, journal, issue, pages, and date, for each category list the following:

a-d) This work has not yet been published. It was mentioned in an oral presentation at the 2013 International Conference on Bio-Nano Innovation, Beijing, "Nanoscale computational science: from materials design to flow and fluctuations", Debra J. Bernhardt.

e) This work has led to a collaboration with Prof Ma Qian, an experimental expert in the fabrication of metal matrix composites and their characterisation using advanced microscopy and powder metal processing at School of Aerospace Mechanical and Manufacturing Engineering, RMIT University, Australia. Debra Bernhardt will also attend the 2014 Low Density Materials Program Review in June 2014 where opportunities for collaboration will be pursued.

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